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APPLICANTS: Takeshi TABATA et al.

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TITLE: NITROGEN OXIDE-REDUCING CATALYST AND PROCESS FOR  
REDUCING NITROGEN OXIDES IN EXHAUST GAS

### **VERIFYING DECLARATION**

Honorable Assistant Commissioner For Patents  
Washington, D.C. 20231

Sir:

I, Hirofumi OHTSUKA, declare and say:

that I am thoroughly conversant in both the Japanese and English languages, and I am presently engaged as a translator in these languages;

that the attached document represents a true English translation of the Japanese Priority document, Japanese Patent Application No.86259/1995 submitted in the U.S. Patent and Trademark Office in connection with the above-identified application.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine of imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 2nd day of November, 1999.

Hirofumi Ohtsuka  
Hirofumi OHTSUKA



PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy  
of the following application as filed with this Office.

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Application Number: Patent Application No. 86259/1995

Applicant: Osaka Gas Company Limited

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Commissioner,

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(Seal)



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Title of the Invention: Nitrogen Oxides Reduction Catalyst and Process for Reducing Nitrogen Oxides in Exhaust Gas

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Inventor:

Address: c/o Osaka Gas Co., Ltd.,  
1-2, Hiranomachi 4-chome, Chuo-ku,  
Osaka-shi

Name: Takeshi Tabata

Inventor:

Address: c/o Osaka Gas Co., Ltd.,  
1-2, Hiranomachi 4-chome, Chuo-ku,  
Osaka-shi

Name: Mikako KOKITSU

Inventor:

Address: c/o Osaka Gas Co., Ltd.,  
1-2, Hiranomachi 4-chome, Chuo-ku,  
Osaka-shi

Name: Osamu OKADA

Inventor:

Address: c/o Osaka Gas Co., Ltd.,  
1-2, Hiranomachi 4-chome, Chuo-ku,  
Osaka-shi

Name: Hirofumi OHTSUKA

Inventor:

Address: Via A.Scoto 44, 29100 Piacenza,



Italy

Name: Giuseppe BELLUSSI

Inventor:

Address: Via Morandi 2/B, San Donato,  
20097 Milanese, Italy

Name: Lugina Maria Flora SABATINO

Applicant:

Identification No.: 000000284  
Name: Osaka Gas Co., Ltd.  
Representative: Shinichiro RYOKI

Agent:

Identification No.: 100085486

Postal Code: 530

Address: Takahashi Bldg. Kita-sangokan  
6th floor, 13-3, Nishitenma 5-chome,  
Kita-ku, Osaka-shi

Patent Attorney  
Name: Takeyoshi HIROSE

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Item:	Specification	1 copy
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- 1 -

Document name: Specification

Title of the invention: Nitrogen Oxides Reduction Catalyst and Process for Reducing Nitrogen Oxides in Exhaust Gas

What is claimed is:

1. A catalyst for reducing nitrogen oxides in an oxygen-rich atmosphere with hydrocarbons, comprising at a minimum crystalline metallosilicate ion exchanged with at least one metal selected from among Mn, Co, Ni, Ag and In, said crystalline metallosilicate having straight channels of oxygen 8-ring or larger sections oriented in at least two different dimensional directions, said straight channels communicating with each other via oxygen 8-ring or larger micropores, the straight channels in at least one of said at least two different dimensional directions having an oxygen 10-ring or larger section.

2. The NOx reducing catalyst according to claim 1, wherein the ion-exchanging metal is Co.

3. The NOx reducing catalyst according to claim 2, wherein the crystalline metallosilicate is aluminosilicate.

4. The NOx reducing catalyst according to claim 2, wherein the crystalline metallosilicate is of either MEL or BEA type.

5. The NOx reducing catalyst according to claim 4, wherein the crystalline metallosilicate is crystalline aluminosilicate with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 10 to 100 and with a Co/Al ratio of 0.2 to 0.6.

6. A process for reducing nitrogen oxides in exhaust gas containing hydrocarbons and an excessive amount of oxygen,

comprising the step of using a catalyst which at a minimum contains crystalline metallosilicate ion-exchanged with at least one metal selected from among Mn, Co, Ni, Ag and In, said crystalline metallosilicate having straight channels of oxygen 8-ring or larger sections oriented in at least two different dimensional directions, said straight channels communicating with each other via oxygen 8-ring or larger micropores, the straight channels in at least one of said at least two different directions having an oxygen 10-ring or larger section.

7. The process for reducing NO<sub>x</sub> in exhaust gas according to claim 6, wherein the catalyst is a catalyst in which the ion-exchanging metal is Co and which contains a crystalline metallosilicate which is of either an MEL or BEA type aluminosilicate.

8. The process for reducing NO<sub>x</sub> in exhaust gas according to claim 7, wherein 90% or more of the hydrocarbons in terms of methane are hydrocarbons having four or smaller number of carbons.

Detailed description of the invention:

[0001]

Industrial Utilization Field:

The present invention relates to a catalyst for reducing nitrogen oxides in exhaust gas, and a process for reducing nitrogen oxides in exhaust gas. More particularly, it relates to a catalyst for reducing nitrogen oxides by using hydrocarbons in exhaust gas containing an excessive amount of oxygen, and to a process for reducing nitrogen oxides in exhaust

gas containing hydrocarbons and an excessive amount of oxygen.

[0002]

Prior art:

As a process for reducing nitrogen oxides (hereinafter referred to as NO<sub>x</sub>) from oxygen-rich exhaust gas, ammonia denitration has been put to practical use. However, this process cannot be applied to small combustors for the following two reasons: firstly, this process requires a storage of an ammonia source, and secondly, slip of excess ammonia causes a secondary environmental pollution problem. It has been found recently, as is disclosed in Japanese Patent Application Laid-Open No. 100919/1988, that NO<sub>x</sub> can be selectively reduced by hydrocarbons on a zeolite catalyst ion-exchanged with a metal like Cu.

[0003]

Problem to be solved by the invention:

However, if hydrocarbons with four or smaller number of carbons are used as the reducing agent, this catalyst has a low selectivity (molar ratio of the hydrocarbons used in NO<sub>x</sub> reduction to the consumed hydrocarbons) in the presence of water vapor which always exists in general exhaust gases, and thus a sufficient NO<sub>x</sub> conversion could not be achieved.

Armor, et al. have reported ("Applied Catalysis B: Environmental," Vol. 1, p. L31) that NO<sub>x</sub> can selectively be reduced by methane on Co ion-exchanged ZSM-5 (MFI zeolite). It is known, however, that the catalytic activity also decreases in the presence of water vapor, so that the catalyst does not

have a sufficient activity for practical use. These problems of the conventional catalysts have urged search for a catalyst which is active even in the presence of water vapor.

The present invention has been made in order to solve the above-mentioned problems. An object of the present invention is to provide an NO<sub>x</sub> reduction catalyst with high durability which is capable of reducing NO<sub>x</sub> from exhaust gas that contains relatively lower hydrocarbons alone as does the exhaust from natural gas combustion, and of providing sufficiently high activity at low temperatures even in exhaust gas containing water vapor, sulfur oxides (hereinafter referred to as SO<sub>x</sub>), etc., and to provide an NO<sub>x</sub> reduction process using this catalyst.

[0004]

Means of solving the problem:

To solve the above-mentioned problems, the present inventors intensively studied catalysts made of crystalline metallosilicate loaded, by ion exchange, with a metal selected from among Mn, Ni, Co, Ag and In. As a result, the inventors found that metal ions dispersed in channels in the crystalline metallosilicate serve as active sites effective in the reaction for the selective catalytic reduction of NO<sub>x</sub> using hydrocarbons consisting of about two to five carbons as the reducing agent, and that active sites deep in the channels also contribute to the reaction, different from the case with a zeolite catalyst loaded with Cu or precious metals. Specifically, in the case of the zeolite catalyst loaded with Cu or precious metals, since



the metal has high oxidation activity, the reaction is completed on the metal or metal ions existing on the zeolite particle surfaces. Even if metal ions are present deep in the channels, they cannot contribute to the reaction. By contrast, the crystalline metallosilicate catalyst loaded with a metal selected from among Mn, Ni, Co, Ag and In is expected to provide high selectivity for NO<sub>x</sub> reduction, due to the low oxidation activity of the metal. However, since the reaction for NO<sub>x</sub> reduction on this catalyst is slow, unreacted reactants enter deep in the channels, thus causing reaction even on metal ions deep in the channels. The catalytic activity may be improved by increasing the concentration of these active sites on the particle surfaces of the support. However, it was also found that, if metal ions are too close to one another, an oxide cluster that can activate oxygen, such as Co<sub>3</sub>O<sub>4</sub>, will be formed, so that the hydrocarbon oxidation activity is enhanced, resulting in lower selectivity of the catalyst and smaller number of active sites.

[0005]

At low temperatures, catalyst such as the Co-ZSM-5 or the like does not provide high activity for selective catalytic reduction of NO<sub>x</sub> by lower hydrocarbons in an atmosphere containing water vapor and SO<sub>x</sub>. The inventors found that this phenomenon is attributed to the following: the water vapor and SO<sub>x</sub> contained in the atmosphere prevent diffusion of reactants and reaction products, and thus active sites deep in the channels are not used effectively. The inventors also found

that, to effectively use the active sites present deep in the channels, the channels must be not only large in diameter but also straight, and that the channels of such structure must be oriented in at least two different dimensional directions and must communicate with each other, so as to form bypasses.

[0006]

The present invention has been made based on these findings. The catalyst according to the present invention comprises crystalline metallosilicate ion-exchanged with at least one metal, selected from among Mn, Co, Ni, Ag and In, to provide active sites, the crystalline metallosilicate having straight channels of oxygen 8-ring or larger sections, directed in at least two different dimensional directions, said straight channels communicating with each other via oxygen 8-ring or larger micropores, the straight channels in at least one direction having an oxygen 10-ring or larger section. The NO<sub>x</sub> reduction process according to the present invention is a process for reducing NO<sub>x</sub> using the above-mentioned catalyst.

[0007]

The crystalline metallosilicate to be used in the present invention has straight channels of oxygen 8-ring or larger sections, which are oriented in at least two different dimensional directions. The straight channels communicate with each other via oxygen 8-ring or larger micropores. The channels in at least one direction have an oxygen 10-ring or larger section. To prevent water vapor and SO<sub>x</sub> from hampering the diffusion of reactants and reaction products, the straight

channels are required to form bypasses. In the case where the straight channels are formed in only one direction like MOR type, reactants can never reach active sites existing in the deeper part of the clogged channels if the channels are clogged with SO<sub>x</sub> etc., which is not suitable.

[0008]

The diffusion rate in the channels differs greatly depending on whether the channels are straight or bent. It is considered that diffusion effective for the reduction of NO<sub>x</sub> in exhaust gas can occur almost only in straight channels. In the case of MFI type metallosilicate in which straight channels are formed in only one direction, if the channels are blocked, it takes too long time to make a detour. Accordingly, it is essential that straight channels be formed in at least two different directions, communicating with each other.

[0009]

If the section of each straight channel is smaller than that of the oxygen 8-ring, reactants, such as NO<sub>x</sub>, hydrocarbons and the like, cannot be diffused into the channels, which is meaningless. The larger is the section of each straight channel, the better, as long as the crystalline metallosilicate has sufficient thermostability. The crystalline metallosilicate having the above-mentioned channel structure includes the types of AFR, AFS, AFY, BEA, BOG, BPH, DAC, FER, GME, HEU, MEL, MFS or OFF, preferably, BEA, BOG or MEL types in which channels are large in diameters. More preferable type is BEA or MEL from the viewpoint that a product

with high purity can be obtained easily. The most preferable form is BEA which has straight channels of oxygen 12-ring sections in two different dimensional directions, the channels communicating with each other via oxygen 12-ring micropores.

[0010]

In addition to the above-mentioned channel structure, the crystalline metallosilicate to be used for the present invention is required to have ion exchange capacity. Crystalline aluminosilicate which is zeolite in a narrow sense, silica aluminophosphate (SAPO), gallosilicate, borosilicate etc. are given as examples of the crystalline metallosilicate with ion exchange capacity. Silicon partly replaced with titanium etc. may also be used. Aluminosilicate is the most preferable in view of the thermostability of crystal and the controllability of ion exchange capacity, although the crystalline metallosilicate of the present invention is not limited to these as long as it has ion exchange capacity.

[0011]

Ion exchange capacity is important because it directly determines the number of active sites. For aluminosilicate, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is a measure for the ion exchange capacity. When the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is higher than 100, the aluminosilicate has insufficient ion exchange capacity so is in short of active sites. When the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is lower than 10, on the other hand, the aluminosilicate increases in hydrophilicity, causing that water hampers reaction for  $\text{NO}_x$  reduction. In addition, an excessive number of cations fill

the channels, narrowing the space, thus impairing the diffusibility. Therefore, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of aluminosilicate is preferably between 10 and 100. For any applicable crystalline metallosilicate other than aluminosilicate, the total number of framework atoms (main element of oxide) per exchangeable monovalent cation is also of a value corresponding to the above-mentioned ratio. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio for stable crystalline metallosilicate is generally fixed for each type of crystalline metallosilicate support. For example, the preferable  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of MEL aluminosilicate is between 20 and 100, and that of BEA aluminosilicate between 10 and 50.

[0012]

The production process of the crystalline metallosilicate to be used for the present invention is not limited as long as the crystalline metallosilicate has ion exchange capacity and straight channels of oxygen 8-ring or larger sections, directed in at least two different dimensional directions, said straight channels communicating with each other via oxygen 8-ring or larger micropores, the straight channels in at least one direction having an oxygen 10-ring or larger section. The crystalline metallosilicate of the above-mentioned structure can be produced, for example, by ordinary hydrothermal synthesis using a template and the like. For example, MEL aluminosilicate can be synthesized by the method disclosed in U.S. Patent No. 3709979, and BEA aluminosilicate by the method disclosed in U.S. Patent No.

3308069.

[0013]

The catalyst of the present invention comprises the above-mentioned crystalline metallosilicate loaded, by ion exchange, with at least one metal selected from among Mn, Ni, Co, Ag and In, more preferably from among Mn, Ni and Co, or most preferably with at least Co. The ion exchange may be carried out by any ordinary method. For example, proton-, sodium- or ammonium-form aluminosilicate is suspended in an aqueous solution in which the water-soluble salt of a metal is dissolved in a quantity equivalent to, or somewhat larger than, the ion exchange capacity, keeping a temperature between room temperature and about 80 °C, to allow ion exchange to take place for an hour to about three days. The resultant product is then washed with water, dried and calcined at temperatures between 400 °C and 750 °C. Since the crystalline metallosilicate has a channel structure suitable for diffusion, ion exchange can be carried out relatively easily. Therefore, it is more preferable to carry out the ion exchange in an aqueous solution at a lower concentration and a lower temperature, because such conditions allow metal ions to be loaded completely on ion-exchange sites without causing aggregation, which is preferable.

[0014]

The preferable metal loading amount is from 40% to 120% in terms of ion exchange rate. The ion exchange rate is the percentage of the sum of products of the molar number of

loaded metal multiplied by the valence of the metal ions, to the ion exchange capacity obtained by summing up the products of the molar number of exchangeable cations multiplied by the valence. If the ion exchange rate is lower than the above-mentioned preferable range, the activity of the catalyst will be insufficient. The ion exchange rate higher than this range is not desirable either: metal ions not only fill the straight channels, narrowing the passage for reactants, but also can be aggregated.

[0015]

The catalyst of the present invention may contain alkaline earth metal as a promoter, and a binder, etc. The catalyst of the present invention may be formed into a pellet or honeycomb form, or may be wash-coated on a refractory honeycomb support. The catalyst of the present invention uses crystalline metallosilicate support on which metal ions having low oxidation activity can be loaded with high dispersion, high selectivity of NO<sub>x</sub> reduction can be obtained. In addition, this metallosilicate has a channel structure suitable for diffusion. Therefore, even in an actual exhaust gas atmosphere containing water vapor and SO<sub>x</sub>, reactants can reach the active sites of metal ions deep in the channels. Accordingly, the catalyst of the present invention has high activity at low temperatures and maintains high selectivity even at high temperatures, which leads to a high NO<sub>x</sub> conversion in a wide range of temperatures. Furthermore, since many bypasses allowing high diffusion are formed in the crystalline metallosilicate in case of possible

partial clogging of the channels, the catalyst of the present invention has high durability.

[0016]

The NOx reduction process of the present invention is a process for selectively reducing NOx in exhaust gas containing hydrocarbons and an excessive amount of oxygen, using hydrocarbons on a catalyst, which process comprises the step of using a catalyst which contains crystalline metallosilicate ion-exchanged with at least one metal selected from among Mn, Co, Ni, Ag and In obtained above, said crystalline metallosilicate having straight channels of oxygen 8-ring or larger sections oriented in at least two different dimensional directions, said straight channels communicating with each other via oxygen 8-ring or larger micropores, the straight channels in at least one of said at least two different directions having an oxygen 10-ring or larger section.

[0017]

The NOx reduction process of this invention comprises allowing the above-mentioned catalyst to contact exhaust gas containing NOx, hydrocarbons and an excessive amount of oxygen. The conditions for this reduction process are not specifically limited as long as the process uses the above-mentioned catalyst containing crystalline metallosilicate ion-exchanged with at least one metal selected from among Mn, Co, Ni, Ag and In, the crystalline metallosilicate having straight channels of oxygen 8-ring or larger sections, oriented in at least two different dimensional



directions, said straight channels communicating with each other via oxygen 8-ring or larger micropores, the straight channels in at least one direction having an oxygen 10-ring or larger section. The operating temperature is between 300 and 600 °C, preferably between 350 and 500 °C, and with a gaseous hourly space velocity (GHSV) between 2,000 and 100,000, preferably between 5,000 and 30,000. When the temperature is lower than 300 °C, the catalytic activity is insufficient. When the temperature is higher than 700 °C, early deterioration of the catalyst is accelerated. Further, the GHSV lower than 2,000 would result in a high-pressure loss, and that higher than 100,000 would result in a poor NO<sub>x</sub> conversion.

[0018]

The hydrocarbons mentioned in the present invention refer to a wide variety of hydrocarbons, including olefins such as ethylene, and paraffins such as propane. Preferably, they should be aliphatic hydrocarbons containing two to five carbons. Aromatic hydrocarbons are not effective very much, because the catalyst of the present invention does not have high activity for hydrocarbon oxidation. With aliphatic hydrocarbons containing about six or more carbons, the advantageous features of the present invention cannot be utilized since the diffusion rate of the hydrocarbons themselves is low. A sufficient NO<sub>x</sub> conversion may not be attained with methane, which has low reactivity at temperatures lower than 400 °C.

[0019]

The NO<sub>x</sub> concentration in exhaust gas is not specifically limited. The hydrocarbon concentration in terms of methane (THC) required for the reduction of NO<sub>x</sub> is, normally, from 1/2 to 10 times the NO<sub>x</sub> concentration. That is, the hydrocarbon concentration required for the reduction of 10 to 5,000 ppm NO<sub>x</sub> is 5 ppm to 5%. If the hydrocarbon content in exhaust gas is not sufficient, an appropriate amount of hydrocarbon may be added to the exhaust gas depending on a desired NO<sub>x</sub> conversion. Since the NO<sub>x</sub> reduction process of the present invention uses the catalyst, which accelerates diffusion in the channels, a high NO<sub>x</sub> conversion can be obtained even at a low NO<sub>x</sub> concentration that is unfavorable to diffusion.

[0020]

If the oxygen concentration in exhaust gas is excessively low, oxidation of NO, the first stage of the reaction, does not occur. The oxygen concentration is preferably 0.5% or higher, more preferably 3% or higher. Although there is no upper limit of the oxygen concentration, the oxygen concentration higher than that of air is not preferable since unexpected explosive combustion can be caused. However, since on the catalyst used in the NO<sub>x</sub> reduction process of the present invention, metal ions having low activity for hydrocarbon oxidation are highly dispersed for a long time, the catalytic selectivity hardly drops in exhaust gas even if the oxygen concentration rises.

[0021]

Exhaust gas may also contain other substances, such as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{SO}_x$  and the like. The  $\text{NO}_x$  reduction process of the present invention is particularly suitable for use in exhaust gas containing water,  $\text{SO}_x$  and the like, which are considered to hamper the reaction for selective catalytic reduction using hydrocarbons. The reduction process of the present invention is also suitable for reducing  $\text{NO}_x$  from exhaust gas produced by combustion of natural gas in which hydrocarbons having four or fewer carbons account for 90% or more of the entire hydrocarbons in terms of methane.

Since the  $\text{NO}_x$  reduction process of the present invention uses hydrocarbons to reduce  $\text{NO}_x$ , hydrocarbons in the exhaust gas are also removed. An oxidation catalyst may be installed downstream of the catalyst of the present invention, if necessary, to oxidize remaining  $\text{CO}$ , hydrocarbons etc.

[0022]

[Examples]

The present invention will be described further in detail with reference to Examples and Comparative Examples. These examples are not to be construed to limit the scope of the present invention.

[0023]

Example 1

BEA aluminosilicate (hereinafter referred to as BEA zeolite) with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 18.87 was prepared by the method disclosed in U.S. Patent No. 3308069. Twenty grams of the resultant BEA zeolite (proton-form) was suspended in 300

ml aqueous solution of 0.2 M cobalt acetate, to carry out ion exchange for 5 hours at 60 °C. The resultant ion-exchanged BEA zeolite was separated by filtration, washed with water, and then underwent ion exchange again in the same manner. The resultant ion-exchanged Co-zeolite was washed with water, dried, and calcined for 5 hours in air at 550 °C, to obtain Co-BEA(1) catalyst. The Co content of this catalyst was 4.01 wt%, the Co/Al ratio was 0.54, and the ion exchange rate was 108%.

[0024]

#### Example 2

Co-BEA(2) catalyst was obtained in the same manner as in Example 1, except that 12g of the BEA zeolite (proton-form) with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 44.08, which was prepared by the method disclosed in U.S. Patent No. 3308069, was suspended in 65 ml aqueous solution of cobalt acetate. The Co content of Co-BEA(2) catalyst was 2.22 wt%, the Co/Al ratio was 0.55, and the ion exchange rate was 110%.

[0025]

#### Example 3

MEL aluminosilicate (hereinafter referred to as MEL zeolite) with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 36.3 was prepared by the method disclosed in U.S. Patent No. 3709979. Co-MEL catalyst was obtained in the same manner as in Example 1, except that 15g of the obtained MEL zeolite (Na-form) was suspended in 105 ml aqueous solution of cobalt acetate. The Co content of the resultant catalyst was 2.78 wt%, the Co/Al ratio was 0.56, and the ion exchange rate was 112%.

[0026]

Comparative Example 1

Co-Y catalyst was obtained in the same manner as in Example 1, except that 30g of FAU aluminosilicate with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 4.8, manufactured by UC company, was suspended in 500 ml aqueous solution of cobalt acetate. The Co content of this catalyst was 8.2 wt%, the Co/Al ratio was 0.32, and the ion exchange rate was 64%.

[0027]

Comparative Example 2

Co-MOR catalyst was obtained in the same manner as in Example 1, except that 5 g of MOR aluminosilicate (hereinafter referred to as MOR zeolite) with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 11.2, manufactured by Norton company, was suspended in 500 ml aqueous solution of 0.03 M cobalt acetate, and that the ion exchange operation was repeated four cycles. The Co content of the obtained catalyst was 5.2 wt%, the Co/Al ratio was 0.37, and the ion exchange rate was 74%.

[0028]

Comparative Example 3

MFI aluminosilicate (hereinafter referred to as MFI zeolite) with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 35 was prepared by the method disclosed in U.K. Patent No. 1402981. Co-MFI(1) catalyst was obtained in the same manner as in Example 1, except that 20g of the obtained MFI zeolite (Na-form) was suspended in 150 ml aqueous solution of cobalt acetate. The Co content of this catalyst was 1.42 wt%, the Co/Al ratio was 0.29, and

the ion exchange rate was 58%.

[0029]

#### Example 4

Each of the catalysts obtained in Examples 1 through 3 and Comparative Examples 1 through 3 was formed into a pellet, which was crushed and sieved to obtain 1 to 2 mm particles. The particles were then calcined for 9 hours at 500 °C to prepare a sample. Four milliliters of this sample was packed in a stainless steel reaction tube manufactured by SUS (14 mm in inside diameter). While test gas of the composition specified in Table 1 was allowed to flow through this reaction tube at a rate of 1 liter/min (GHSV = 15,000), the gas composition at the outlet of the reaction tube was measured by a chemiluminescence NOx meter and by a gas chromatograph.

[0030]

[Table 1]

NO = 500 ppm	H <sub>2</sub> = 660 ppm
C <sub>3</sub> H <sub>8</sub> = 1000 ppm	CO <sub>2</sub> = 6 %
O <sub>2</sub> = 10 %	H <sub>2</sub> O = 9 %
CO = 1000 ppm	He balance

[0031]

Table 2 gives the catalytic activity (NOx and propane conversions) of each catalyst at 400 °C and 500 °C. The NOx and propane conversions were calculated from the NOx and propane concentrations at the inlet and outlet of the reaction

tube, using the following equations:

[0032]

$$\text{NOx Conv. (\%)} = \frac{\text{Outlet N}_2 \text{ Conc. (ppm)}}{\text{Inlet NO Conc. (ppm)}} \times 100$$

$$\text{C}_3\text{H}_8 \text{ Conv. (\%)} = \frac{\text{Outlet (CO+CO}_2\text{) Conc. (ppm)}}{\text{Inlet NO Conc. (ppm)}} \times 100$$

[0033]

[Table 2]

Catalyst	NOx Conversion (C <sub>3</sub> H <sub>8</sub> Conversion) (%)	
	400 °C	500 °C
Co-BEA(1)	80.4 (100)	64.7 (100)
Co-BEA(2)	83.4 (99.8)	73.4 (100)
Co-MEL	77.7 (90.5)	65.9 (100)
Co-Y	0 (1.9)	3.9 (51.2)
Co-MOR	54.2 (91.1)	35.4 (100)
Co-MFI(1)	56.8 (94.1)	46.6 (100)

[0034]

As is apparent from Table 2, the Co-BEA(1), Co-BEA(2) and Co-MEL catalysts according to the present invention have high NOx conversions at 400 °C indicating that they have high activity at low temperatures. Their NOx conversions drop only a little at 500 °C, which verifies that these catalysts maintain high selectivity for NOx reduction even at high temperatures.

[0035]

Example 5

Co-BEA(3) catalyst was obtained in the same manner

as in Example 1, except that 15g of BEA zeolite (Na-form) with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 19.7, which was prepared by the method disclosed in U.S. Patent No. 3308069, was suspended in 60 ml aqueous solution of cobalt acetate. The Co content of this catalyst was 1.82 wt%, the Co/Al ratio was 0.21, and the ion exchange rate was 42%.

The activity of this catalyst was evaluated in the same manner as in Example 4. The NOx conversion at 400°C was 66%. The durability of this catalyst was also evaluated in the same manner as in Example 4, except that a test gas having the composition shown in Table 3, which simulates the exhaust of a lean burn natural gas engine, was continuously allowed to flow (GHSV=1500). The results thereof are shown in Fig. 1. The NOx and  $\text{C}_3\text{H}_8$  conversions are the values defined in the same manner as in Example 4.

[0036]

[Table 3]

NO = 150 ppm	H <sub>2</sub> = 660 ppm
C <sub>3</sub> H <sub>8</sub> = 500 ppm	CO <sub>2</sub> = 6 %
O <sub>2</sub> = 10 %	H <sub>2</sub> O = 9 %
CH <sub>4</sub> = 1000 ppm	SO <sub>2</sub> = 0.3 ppm
CO = 500 ppm	He balance

[0037]

As is obvious from Fig. 1, the Co-BEA (3) catalyst constantly maintained a 60% or higher NOx conversion for 2,000



hours, verifying that the catalyst of the present invention not only provides high initial activity but high durability even in an atmosphere containing water vapor and SOx.

[0038]

#### Example 6

The durability of the Co-MEL catalyst obtained in Example 3 was evaluated in the same manner as in Example 5. The catalyst was stable in activity and had about a 50% NOx conversion after the lapse of 500 hours.

[0039]

#### Comparative Example 4

The durability of the Co-MOR catalyst obtained in Comparative Example 2 was evaluated in the same manner as in Example 5. As a result, the catalytic activity deteriorated substantially in 24 hours, with the NOx conversion dropping below 20%. Therefore, the operating temperature was raised to 450 °C. Although the conversion rate recovered temporarily, its declining tendency did not change, dropping below 10% in 140 hours. Thus, it is seen that the Co-MOR catalyst has no durability for practical use.

[0040]

#### Comparative Example 5

Co-MFI(2) catalyst ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$ ) was obtained substantially in the same manner as in Comparative Example 3. The Co content was 1.9 wt%, the Co/Al ratio was 0.53, and the ion exchange rate was 106%.

The activity of this catalyst was evaluated in the

same manner as in Example 4. The catalyst had a 68% NOx conversion at 400 °C. The durability was also evaluated in the same manner as in Example 5. However, as shown in Fig. 2, the catalytic activity deteriorated substantially with time, and the NOx conversion dropped below 20% in 500 hours. These evaluation results indicate that the Co-MFI catalyst is not sufficiently durable in an actual operating atmosphere although its initial activity is moderately high.

[0041]

#### Comparative Example 6

Five grams of BEA zeolite (proton-form) with an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 22.3 was suspended in 1,000 ml aqueous solution of 0.0035 M copper acetate, to carry out ion exchange for 18 hours at room temperature. The resultant ion-exchanged Cu-BEA zeolite was washed with water, dried, and calcined for 9 hours at 500 °C, to obtain Cu-BEA catalyst. The Cu content of the obtained catalyst was 4.0 wt%, the Cu/Al ratio was 0.53, and the ion exchange rate was 107%.

The durability of this catalyst was evaluated in the same manner as in Example 5, except that the operating temperature was 500 °C. As shown in Fig. 3, this catalyst provides poor selectivity for NOx reduction, and the activity continues decreasing even after the lapse of 600 hours. This activity deterioration is presumably caused by aggregation of Cu ions as in the case with the Cu-ZSM-5 (Cu-MFI) catalyst, also reported by the inventors ("Study on Surface Science and Catalysis," Vol. 88, p. 409). Thus, if ion-exchanged with Cu,

the BEA catalyst cannot be expected to show an improvement in NO<sub>x</sub> conversion, nor can it have a greater suppression effect on Cu ion aggregation, compared with the MFI catalyst.

[0042]

#### Example 7

Co-BEA(4) catalyst was obtained in the same manner as in Example 1, except that 250.14 g of BEA zeolite (Na-form) with an SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 22.3 was suspended in 2,000 ml aqueous solution containing 1,000 ml cobalt acetate. The Co content of the resultant catalyst was 3.0 wt%, the Co/Al ratio was 0.40, and the ion exchange rate was 80%.

The durability of this catalyst was evaluated in the same manner as in Example 5, except that, as a test gas, the exhaust gas discharged from a natural gas-fueled cogeneration system (air/fuel ratio = approx. 1.4), having the average composition shown in Table 4, and to which C<sub>3</sub>H<sub>8</sub> was added to give a concentration of 1,000 ppm, was allowed to flow at a rate of 10 liter/min (GHSV = 15,000) at 450 °C through the reaction tube packed with 40 ml of the catalyst sample. Fig. 4 shows the results of the evaluation.

[0043]

[Table 4]

NO = ca. 500 ppm	CO = ca. 800 ppm
THC = ca. 2200 ppm (including CH <sub>4</sub> = ca. 1600 ppm)	
CO <sub>2</sub> = ca. 8.5 %	SO <sub>2</sub> = ca. 0.4 ppm
O <sub>2</sub> = ca. 6 %	H <sub>2</sub> O = ca. 13 %

[0044]

As is apparent from Fig. 4, even in actual engine exhaust gas, this catalyst showed a 60% or higher NOx conversion for 1,500 hours, with slight variation due to fluctuation in the air/fuel ratio of the combustion in the engine.

[0045]

Effect of the invention:

According to the catalyst of the present invention, since a metal with low activity for hydrocarbon oxidation is used, it provides high selectivity for NOx reduction. In addition, its crystalline metallosilicate is used as a support on which metal ions can be loaded with high dispersion. Furthermore, straight channels of large sections, oriented in two or more different dimensional directions and communicating with each other, are formed in this crystalline metallosilicate support, enabling reactants to be diffused at a very high rate. Consequently, the metal ions (active sites) existing deep in the straight channels are also used effectively, and thus high activity in NOx reduction is achieved even at low temperatures. Further, since the NOx reduction process according to the present invention uses the above-mentioned catalyst, it effects a high NOx conversion in a wide range of temperatures and also even under the conditions unfavorable to diffusion in channels, such as a low NOx concentration or coexisting of detrimental substances such as water vapor, SOx and the like.

Brief description of the drawings:

Fig. 1 shows the durability of the catalyst of the

present invention (Example 5).

Fig. 2 shows the durability of the catalyst of the comparative example (Comparative example 5).

Fig. 3 shows the durability of the catalyst of the comparative example (Comparative example 6).

Fig. 4 shows the durability of the catalyst of the present invention (Example 7).

Document name:

Drawings

Fig. 1

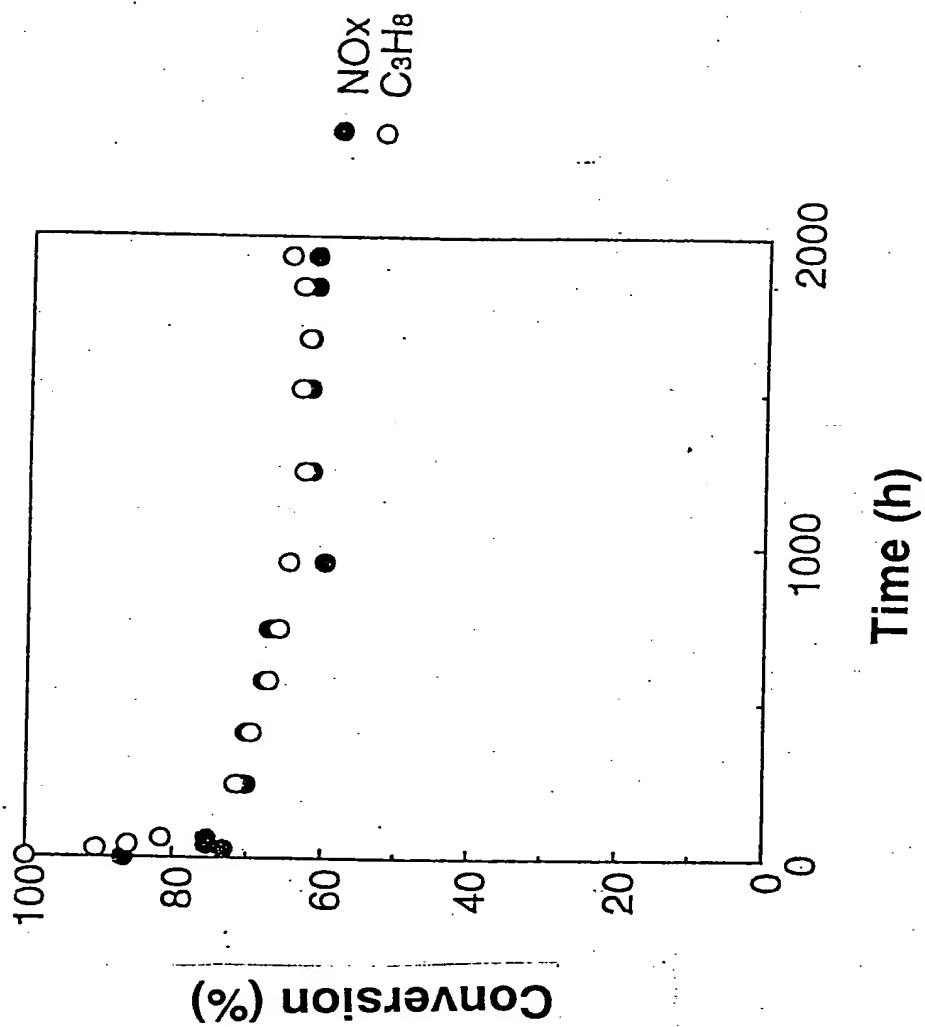


Fig. 2

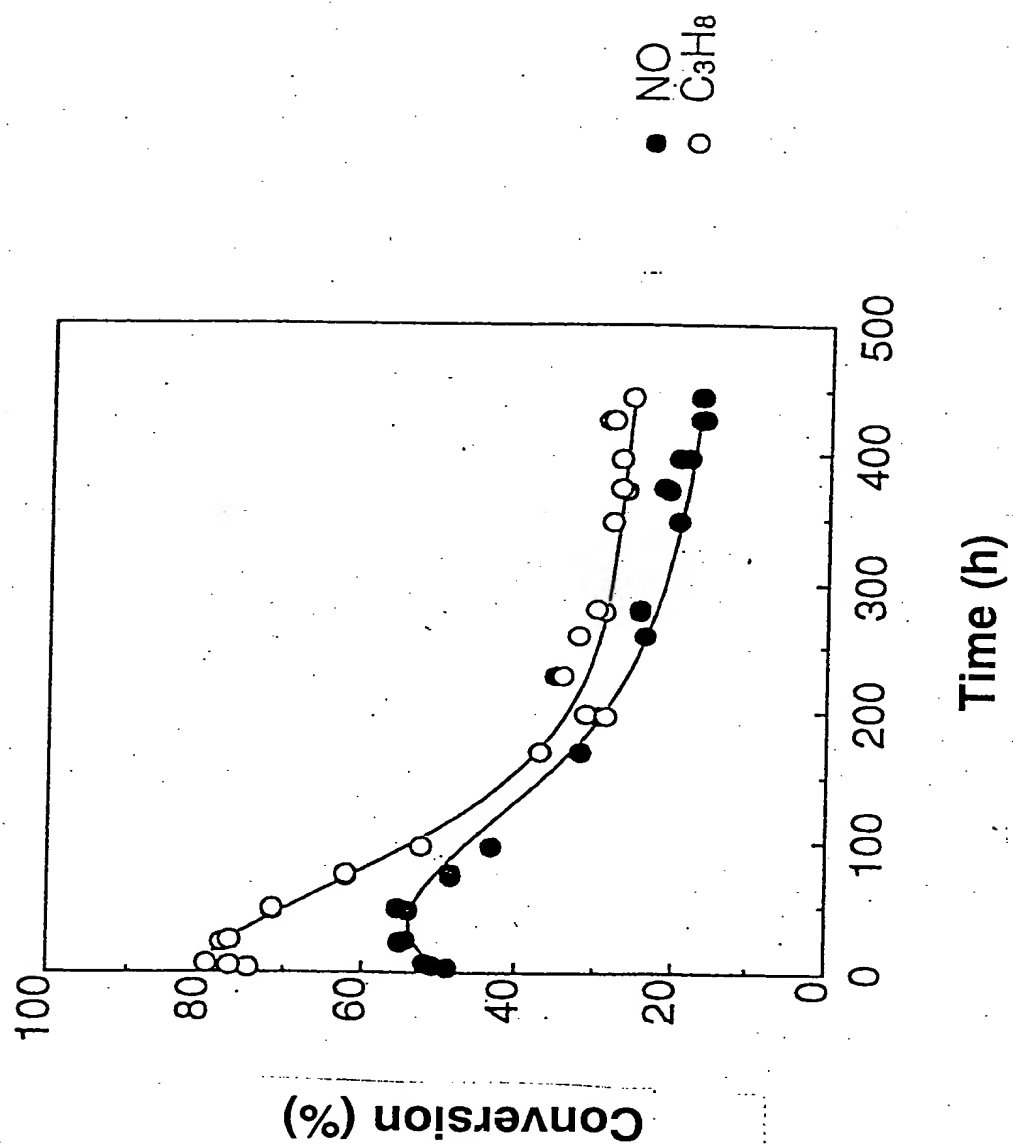


Fig. 3

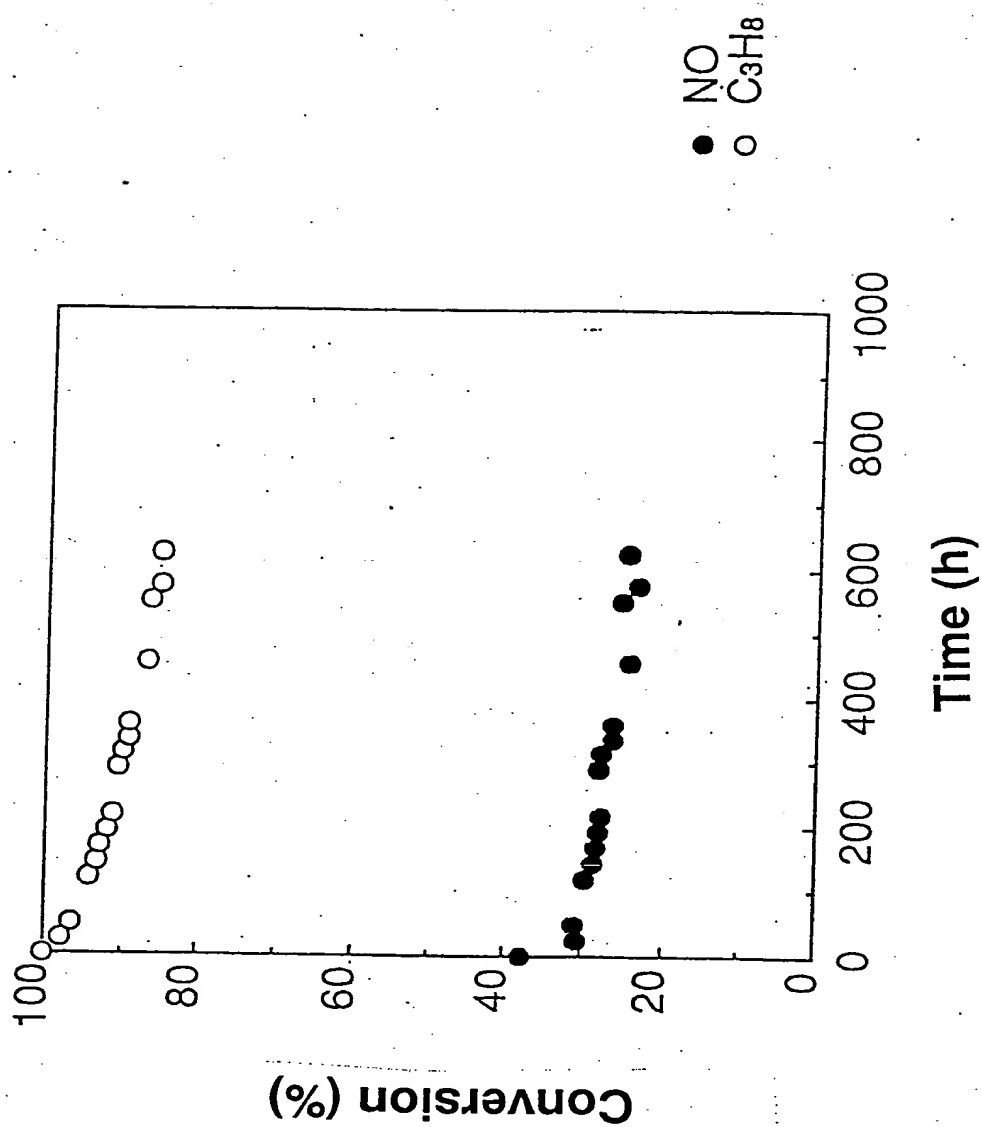
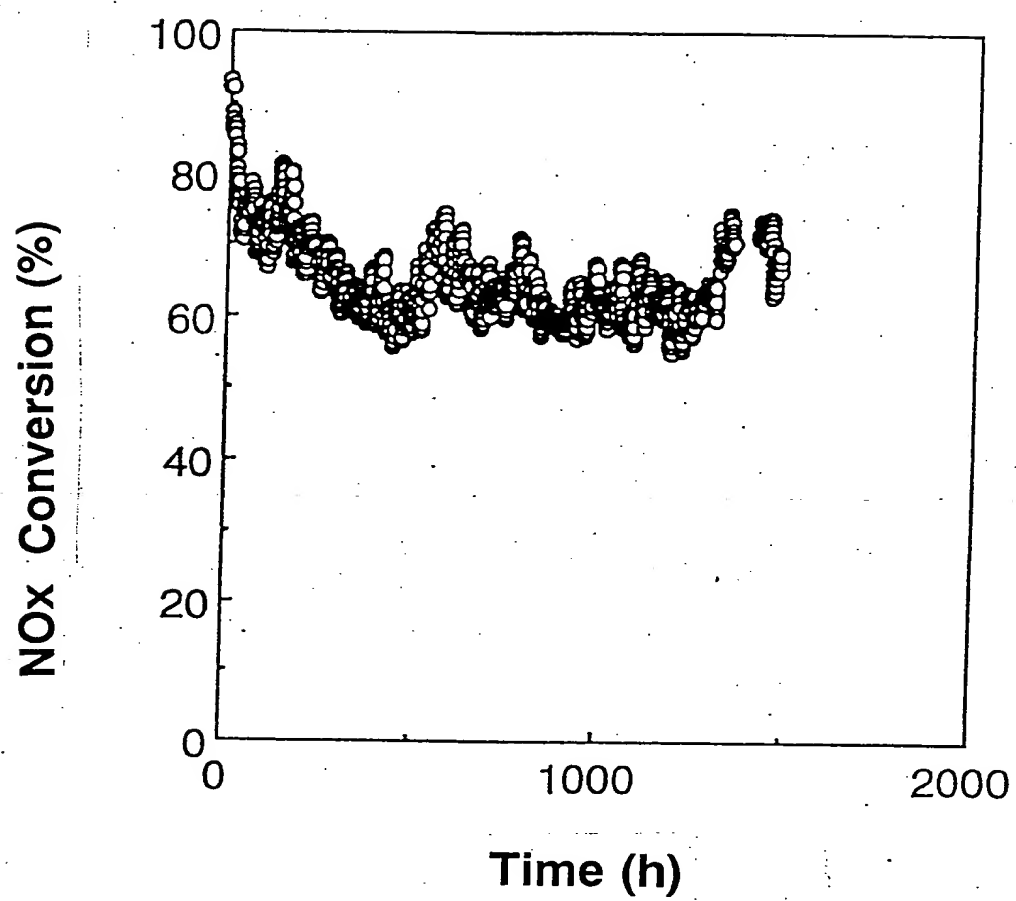




Fig. 4





Document name: Abstract

Summary:

Object: To provide a catalyst for reducing nitrogen oxides (NOx) in exhaust gas, and an NOx reduction process using said catalyst.

Constitution: The NOx reducing catalyst of the present invention at a minimum comprises crystalline metallosilicate ion-exchanged with at least one metal selected from among Mn, Co, Ni, Ag and In, and which has channels of a specific structure. The NOx reduction process of the present invention comprises using said catalyst.

Since a metal having low activity for hydrocarbon oxidation, the catalyst provides high selectivity for NOx reduction. In addition, since the catalyst comprises channels of a specific structure, metal ions (active sites) existing deep in the channels are utilized effectively, thus providing high NOx reduction activity even at low temperatures.

Selected figure: None



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Applicant:

Identification No.: 000000284

Address: 1-2, Hiranomachi 4-chome,  
Chuo-ku, Osaka-shi, Osaka-fu

Name: Osaka Gas Co., Ltd.

Agent: Applicant

Identification No.: 100085486

Address: Takahashi Bldg. Kita-sangokan  
6th floor, 13-3, Nishitenma  
5-chome, Kita-ku, Osaka-shi,  
Osaka-fu

Name: Takeyoshi HIROSE



Applicant Record

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Address: 1-2, Hiranomachi 4-chome,  
Chuo-ku, Osaka-shi, Osaka-fu

Name: Osaka Gas Co., Ltd.